

Chapter 3 - Entropy (and probability)

See pages
671-681

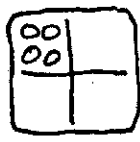
↳ "Number of ways of arranging"

Thermodynamics derives directly from a statistical treatment of particles and their energies.

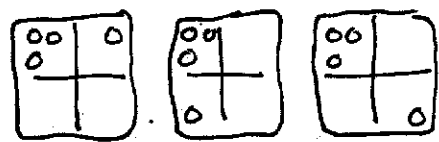
Equilibrium is simply the statistically most likely outcome.

Imagine a flat pan divided into 4 equal quadrants, each capable of holding 4 marbles.
Now place 4 marbles in the pan

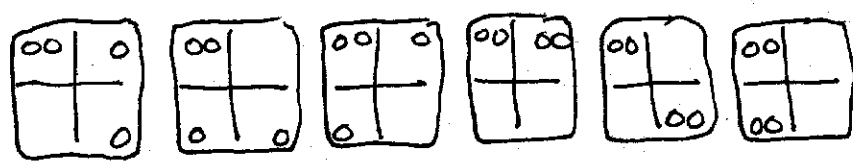
4 top left



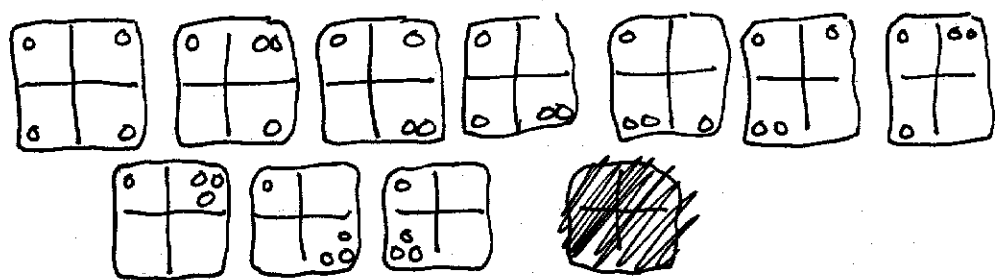
3 top left



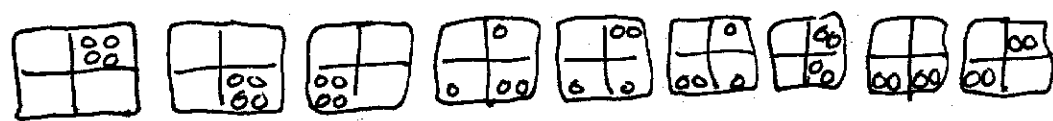
2 top left



1 top left



0 top left



All arrangements
equally likely!

If I start off with all the balls in the top left quadrant and shake the pan,

how likely is it that when everything settles, all the balls will be in the top left quadrant?

Intuition $\Rightarrow$ Not likely at all! $\Leftarrow$ 2ND LAW

Why? Using statistics, we see that there is only one way to put 4 balls in upper left quadrant.

There are lots of other ways to arrange the balls. If all ways equally probable, then unlikely to return to that one state.

(with enough enthalpy (my hand) we can force the balls back to that state!)

Now, if the pan is tilted slightly down to the left, then some configs are more probable than others. We've changed the energy of some of the possible states relative to the others.

If we now require the total energy of the balls to equal some energy, then we have fewer ways of arranging.

The most probable distribution is the one with the largest number of ways of being formed.

Imagine the box with 4 quadrants, each capable of holding 10^6 balls. Each quadrant has slightly different heights (a ball has slightly lower energy in the deepest, higher in the highest).

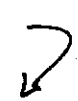
Shake the box and let it settle. How are balls distributed?

$$\text{Boltzmann showed } \Rightarrow \frac{N_i^0}{N} = \frac{e^{-E_i^0/kT}}{\sum_i e^{-E_i/kT}}$$

(~~each~~ a ball in each of the 4 quadrants has energy E_1, E_2, E_3 , or E_4 (E_i^0)).

$$\text{Fraction of balls in quadrant 1 } \Rightarrow \frac{N_1}{N} = \frac{e^{-E_1/kT}}{\sum_i e^{-E_i/kT}}$$

If two quadrants have the same energy, we say they are degenerate.

Fraction of balls with a certain energy E_i^0 

$$\frac{N_i^0}{N} = \frac{g_i e^{-E_i/kT}}{\sum_i g_i e^{-E_i/kT}}$$

g_i = degeneracy of energy level ①.

So thermo deals with probabilities of finding the system in a state with a specific energy.

Entropy $\Rightarrow$ related to the number of ways of distributing molecules in a system.

Boltzmann
also $\rightarrow$

$$S = k \ln N$$

$N = \#$ of ways of arranging

For our original pan (equal energy-quadrants)

$N = 1$ for all balls top left

$N = 3$ for 3 balls top left etc.

Ordered deck of cards: $A\heartsuit, A\spadesuit, A\diamondsuit, A\clubsuit, 2\heartsuit, 2\spadesuit, 2\diamondsuit, 2\clubsuit, \text{etc}$

$$N = 1$$

Throw them on the ground and let a 3 year old play with them $\rightarrow$ disorder (lots of way of arranging).

Shuffle. Give to 3 year old. How likely is it that the deck will return to original order?
VERY UNLIKELY!

2ND Law

$\rightarrow$ The entropy of the universe always increases.

$$S (\text{ordered}) = k \ln 1 = 0$$

$$S (\text{disordered}) = k \ln 52! = 2.1 \times 10^{21} \text{ J/K}^{-1}$$

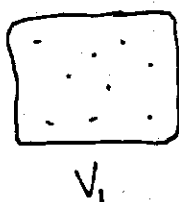
A pure, perfect crystal at 0K has 1 microstate.
~~Entropy~~ (only one way to order)

$$S = k \ln 1 = 0$$

3RD LAW.

Also defines the
Kelvin temperature
Scale.

An ideal gas at constant T , but different V (volumes).



There are fewer ways to
arrange the gas molecules
in V_2 than in V_1

Entropy of an ideal gas depends on volume

To reduce the volume (and $\therefore$ to reduce the entropy),
we must do work on the system

→ In the same way that we had to do work
to re-order a dis-ordered deck of cards.

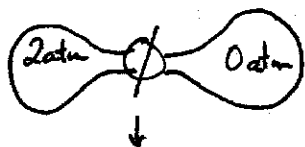
The first part of Chapter 3 convinces us that

$$\Delta S = \frac{q_{REV}}{T}$$

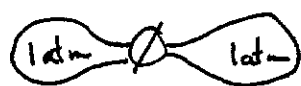
is a state variable.
(an extensive one)

(for T measured in K).

Surroundings...



One mole of an ideal gas expands from P_1, V_1, T_1 to P_2, T_1 , and $2V_1$ (isothermal).
(i.e. it doubles in volume).



- a) expansion is irreversible into a vacuum ($w=0$)
b) expansion is reversible what is ΔS for (a)?

a) $P_{ext} = 0$. Therefore $-P\Delta V = 0 = w$

Temperature did not change. $\therefore \Delta E = 0$.

$$\Delta E = q + w \Rightarrow 0 = q_{irrev} + 0$$

$$\therefore q_{irrev} = 0$$

$$\therefore \Delta S_{surroundings} = 0$$

No heat or work exchanged with surroundings

Makes sense $\Rightarrow$ _____

Stop 9/20

Now, what is ΔS_{system} ?

$$\Delta S_{system} = \frac{q_{REV}}{T}$$

(so have to look at reversible path)

$$W_{REV} = - \int_{V_1}^{V_2} P dV = - nRT \ln \frac{V_2}{V_1} \quad (\text{homework})$$

$$= -(1 \text{ mol}) (RT) \ln 2 = -RT \ln 2$$

BUT

$$\Delta E = 0 = q_{REV} + (-RT \ln 2) \quad (\text{for 1 mole})$$

$$\therefore q_{REV} = RT \ln 2$$

$$\therefore \Delta S_{sys} = \frac{q_{REV}}{T} = \frac{RT \ln 2}{T} = R \ln 2$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$= R \ln 2 + 0$$

$$= R \ln 2$$

For the isothermal expansion

$$\Delta S_{universe} > 0 \quad \underline{\underline{2ND LAW}}$$

For the reversible expansion, $q_{REV} = RT \ln 2$

How to make it reversible? If the heat is transferred reversibly from the ~~surroundings~~ ^{system} to the ~~surroundings~~ ^{system} ($q_{REV} > 0$)

How to achieve heat transfer reversibly? Temp difference between system and surroundings must be very small at each point along way ($T \approx \text{const}$)

ach!

For the surroundings, ~~heat~~
 heat input to the surroundings = $-q_{\text{REV}}$

$$\therefore \Delta S_{\text{surroundings}} = \frac{-q_{\text{REV}}}{T} = -R \ln 2$$

$\therefore$ ~~System~~

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

$(+R \ln 2) \quad \quad (-R \ln 2)$

Consistent with

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

Real statement
of 2nd law.